(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 205 960**
A2

(12) EUROPEAN PATENT APPLICATION

(21) Application number: **86107119.9**

(51) Int. Cl.⁴: **D01F 6/04**

(22) Date of filing: **26.05.86**

(30) Priority: **17.06.85 US 745164**

(43) Date of publication of application:
30.12.86 Bulletin 86/52

(84) Designated Contracting States:
DE FR GB IT NL

(71) Applicant: **ALLIED CORPORATION**
Columbia Road and Park Avenue P.O. Box 2245R (Law Dept.)
Morristown New Jersey 07960(US)

(72) Inventor: **Dunbar, James Jay**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Kavesh, Sheldon (NMN)**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Prevorsek, Dusan Ciril**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Tam, Thomas Yiu-Tai**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Weedon, Gene Clyde**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Winckhofer, Robert Charles**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)

(74) Representative: **Brullé, Jean et al**
Service Brevets Bendix 44, rue François 1er
F-75008 Paris(FR)

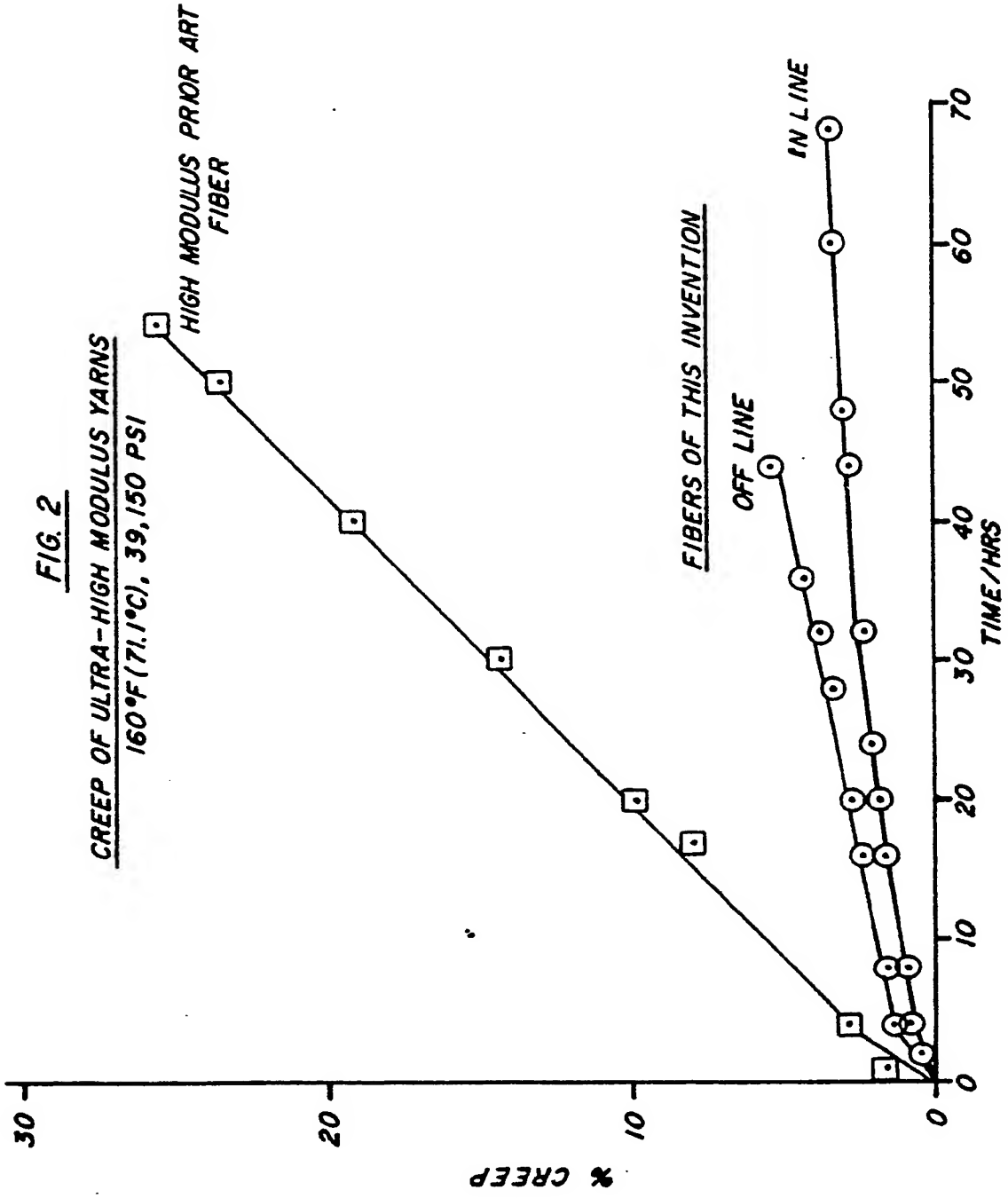
(54) Very low creep, ultra high modules, low shrink, high tenacity polyolefin fiber having good strength retention at high temperatures and method to produce such fiber.

(57) By poststretching, at a temperature between about 135° and 160°C, a polyethylene fiber, which has already been oriented by drawing at a temperature within 5°C of its melting point, an ultra high modulus, very low creep, low shrink, high tenacity polyolefin fiber having good strength retention at high temperatures is obtained. The poststretching can be in multiple stages and/or with previous annealing. The poststretching should be done at a draw rate of less than 1 second^{-1}. Tensile modulus values over 2,000 g/d (178.6 GPa) for multifilament yarn are consistently obtained for ultrahigh molecular weight polyethylene, with tensile strength values above 30 g/d (2.5 GPa) while at the same time dramatically improving creep [at 160°F (71.1°C) and 39,150 psi (2758.3 kg/cm²) load] by values at least 25% lower than fiber which has not been poststretched. Shrinkage is improved to values less than 2.5% of the original length when heated from room temperature to 135°C. Performance at higher temperature is improved by about 15° to 25°C.

EP 0 205 960 A2

FIG. 2

CREEP OF ULTRA-HIGH MODULUS YARNS
160°F (71.1°C), 39,150 PSI



VERY LOW CREEP, ULTRA HIGH MODULUS, LOW SHRINK, HIGH TENACITY POLYOLEFIN FIBER HAVING GOOD STRENGTH RETENTION AT HIGH TEMPERATURES AND METHOD TO PRODUCE SUCH FIBER

BACKGROUND OF THE INVENTION

This invention relates to very low creep, ultra high modulus, low shrink, high tenacity polyolefin fiber having good strength retention at high temperatures and the method to produce such fiber. U.S. Patent 4 413 110, hereby incorporated by reference, in toto, discloses a prior art fiber and process which could be a precursor process and fiber to be poststretched by the method of this invention to create the fiber of this invention.

Although a tensile strength value of 4.7 GPa (~ 55 g/d) has been reported for a single crystal fibril grown on the surface of a revolving drum from a dilute solution of ultra high molecular weight polyethylene, and separately, a tensile modulus value of 220 GPa (~ 2600 g/d) for single crystal mats of polyethylene grown from dilute solution and subsequently stretched in two stages to about 250 times original; the combination of ultra high modulus and high tenacity with very low creep, low shrinkage and much improved high temperature performance has never before been achieved, especially in a multifilament, solution spun, continuous fiber by a commercially, economically feasible method.

SUMMARY OF THE INVENTION

This invention is a polyolefin shaped article having a creep rate, measured at 160°F (71.1°C) and 39,150 psi (2758.3 kg/cm²) load, at least one half the value given by the following equation: percent per hour = $1.11 \times 10^{10}(IV)^{-2.78}$ (Modulus)$^{-2.11}$ where IV is intrinsic viscosity of the article measured in decalin at 135°C, in deciliter per gram, and Modulus is the tensile modulus of the article measured in grams per denier for example by ASTM 885-81, at a 110% per minute strain rate, and at 0 strain. See U.S. 4 436 689, hereby incorporated by reference, in toto, column 4, line 34, for a similar test. Preferably the article is a fiber. Preferably the fiber is a polyolefin. Preferably the polyolefin is polyethylene. Most preferred is a polyethylene fiber.

This invention is also a high strength, high modulus, low creep, high molecular weight polyethylene fiber which has been poststretched to achieve at least about a 10 percent increase in tensile modulus and at least about a 20 percent decrease in creep rate meassured at 160°F - (71.1°C) and a 39,150 psi (2758.3 kg/cm²) load.

Another embodiment of this invention is a high strength, high modulus, low creep, high molecular weight, polyethylene fiber which is poststretched to achieve at least about 20 percent decrease in creep rate measured at 160°F (71.1°C) under 39,150 psi (2758.3 kg/cm²) load, and a retention of the same tenacity as the same fiber, before poststretching, at a temperature at least about 15°C higher. This fiber preferably has a total fiber shrinkage, measured at 135°C, of less than about 2.5 percent. The fiber of the invention also preferably has a tenacity at least about 32 grams per denier - (2.77 GPa) when the molecular weight of the fiber is at least 800,000. On the other hand, when the weight average molecular weight of the fiber is at least about 250,000, tenacity is preferred to be at least about 20 grams per denier (1.73 GPa).

Another embodiment is a high strength, high modulus, low creep, high molecular weight polyethylene fiber which has been poststretched to achieve about 10 percent increase in tensile modulus and a retention of the same tenacity in the same fiber, before poststretching, at a temperature at least about 15° higher.

A futher embodiment is a high strength, high modulus, low creep, low shrink, high molecular weight polyethylene poststretched multifilament fiber having any denier for example between about 5 and 1,000,000, weight average molecular weight at least about 800,000, tensile modulus at least about 1,600 grams per denier (133.7 GPa) and total fiber shrinkage less than 2.5 percent at 135°C. The fiber preferably has a creep of less than 0.48 percent per hour at 160°F (71.1°C), 39,150 psi (2758.3 kg/cm²). When the fiber has been efficiently poststretched the tenacity of the same fiber before it is poststretched is preferably the same at a temperature at least about 25° higher.

The process of this invention is a method to prepare a low creep, high strength, high modulus, high molecular weight polyethylene fiber comprising drawing a highly oriented, high molecular weight polyethylene fiber at a temperature within about 10°C, preferably about 5°C, of its melting temperature then poststetching the fiber at a temperature within about 10°C, preferably about 5°C, of its melting point at a drawing rate of less than 1 second^{-1} and cooling said fiber under tension sufficient to retain its highly oriented state. By melting point is meant the temperature at which the first principal endotherm is seen which is attributable to the major constituent in the fiber, for polyethylene, generally 140° to 151°C. A typical measurement method is found in Example 1. Preferably the fiber

is originally formed by solution spinning. The preferable poststretch temperature is between about 140 to 153°C. The preferred method creates a poststretched fiber with an increased modulus of at least 10 percent and at least about 20 percent less creep at 160°F (71.1°C) and 39,150 psi (2758.3 kg/cm^2) load in the unstretched fiber. It is preferred to maintain tension on the fiber during cooling of the fiber to obtain its highly oriented state. The preferred tension is at least 2 grams per denier. It is preferred to cool the fiber to at least below 90°C, before poststretching.

In the method of this invention it is possible to anneal the fiber after cooling but before poststretching at a temperature between about 110° and 150°C for a time of at least about 0.2 minutes. Preferred annealing temperature is between about 110° and 150°C for a time between about 0.2 and 200 minutes. The poststretching method of this invention may be repeated at least once or more.

By drawing rate is meant the drawing velocity difference divided by the length of the drawing zone. For example if fiber or yarn being drawn is fed to the draw zone of ten meters at ten meters per minute and withdrawn at a rate of twenty meters per minute; the drawing rate would be (20 m/m-10 m/m) divided by 10 m which equals one minute^{-1} or 0.01667 second^{-1}. See U.S. 4 422 993, hereby incorporated by reference, in totocolumn 4, lines 26 to 31.

DETAILED DESCRIPTION OF THE INVENTION

The fiber of this invention is useful in sailcloth, marine cordage, ropes and cables, as reinforcing fibers in thermoplastic or thermosetting resins, elastomers, concrete, sports equipment, boat hulls and spars, various low weight, high performance military and aerospace uses, high performance electrical insulation, radomes, high pressure vessels, hospital equipment and other medical uses, including implants, sutures, and prosthetic devices.

The precursor or feed yarn to be poststretched by the method of this invention can be made by the method of U.S. Patent 4 551 296 or U.S. Patent 4 413 110 or by higher speed methods described in the following examples. The feed yarn could also be made by any other published method using a final draw near the melt point, such as in U.S. 4 422 933.

Example 1

Preparation of Feed Yarn From Ultra High Viscostiy Polyethylene

A 19 filament polyethylene yarn was prepared by the method described U.S. Patent 4 551 296. The starting polymer was of 26 IV (approximately 4 x 10^6 MW). It was dissolved in mineral oil at a concentration of 6 wt.% at a temperature of 240°C. The polymer solution was spun through a 19 filament die of 0.040" (0.1016 cm) hole diameter. The solution filaments were stretched 1.09/1 prior to quenching. The resulting gel filaments were stretched 7.06/1 at room temperature. The extracted and dried xerogel filaments were stretched 1.2/1 at 60°C, 2.8/1 at 130°C and 1.2/1 at 150°C. The final take-up speed was 46.2 m/m. This yarn, possessed the following tensile properties:

258	denier
28.0	g/d tenacity (2.43 GPa)
982	g/d modulus (85.1 GPa)
4.1	elongation

Measurements of the melting temperatures of the precusor yarn were made by differential scanning calorimetry (DSC) using a Perkin-Elmer DSC-2 with a TADS Data Station. Measurements were made on 3 mg unconstrained samples, in argon at a heating rate of 10°C/min. The DSC measurements showed multiple melting endotherms with the main melting point peak at 146°C, 149°C and 156°C in 3 determinations.

Example 2

Preparation of Feed Yarn From High Viscosity Polyethylene

A 118 filament yarn was prepared by the method described in U.S. Serial Number 690 914. The starting polymer was of 7.1 IV (approximately 630,000 MW). It was dissolved in mineral oil at a concentration of 8 wt.% at a temperature of 240°C.

The polymer solution was spun through a 118 filament die of 0.040" (0.1016 cm) hole diameter. The solution filaments were stretched 8.49/1 prior to quenching. The gel filaments were stretched 4.0/1 at room temperature. The extracted and dried xerogel filaments were stretched 1.16/1 at 50°C, 3.5/1 at 120°C and 1.2/1 at 145°C. The final take-up speed was 86.2 m/m. This yarn possessed the following tensile properties:

203	denier
20.3	g/d tenacity (1.8 GPa)
782	g/d modulus (69.8 GPa)
4.6%	elongation

DSC measurements on this precusor yarn showed a double endotherm with the main melting peak at 143°C and 144°C in duplicate determinations.

Example 3

Preparation of Feed Yarn From Ultra High Viscosity Polyethylene at Higher Speeds

A 118 filament polyethylene yarn was prepared by the method described in U.S. Patent 4 413 110 and Example 1 except stretching of the solvent extracted, dry yarn was done in-line by a multiple stage drawing unit having five conventional large Godet draw rolls with an initial finish applicator roll and a take-up winder which operates at 20 to 500 m/m typically in the middle of this range. However, this rate is a balance of product properties against speed and economics. At lower speeds better yarn properties are achieved, but at higher speeds the cost of the yarn is reduced in lieu of better properties with present know-how. Modifications to the process and apparatus described in U.S. Patent 4 413 110 are described below.

After the partially oriented yarn containing mineral oil is extracted by trichlorotrifluoroethane - (TCTFE) in a washer, it is taken up by a dryer roll to evaporate the solvent. The "dry partially oriented yarn" is then drawn by a multiple stage drawing unit. The following is a detailed example of the drawing process.

Yarn from the washer containing 80% by weight TCTFE is taken up by the first dryer roll at constant speed to insure denier control and to provide first stage drying to about 5% of TCTFE. Drawing between dryer rolls at a temperature of about 110°C ± 10 is at 1.05 to 1.8 draw ratio with a tension generally at 4,000 ± 1,000 gms.

A typical coconut oil type finish is applied to the yarn, now containing about 1% by weight TCTFE, as it leaves the second dryer roll, for static control and optimal processing performance. The draw ratio between the second dryer roll at about 60°C and the first draw roll is kept at a minimum - (1.10 -1.2 D.R.) because of the cooling effect of the finish. Tension at this stage is generally 5500 ± 1000 gm.

From the first draw roll to the last draw roll maximum draw at each stage is applied. Yarn is drawn between the first draw roll and the second draw roll (D.R. 1.5 to 2.2) at 130 ± 5°C with a tension of 6000 ± 1000 gm. In the following stage - (second roll and third roll), yarn is drawn at an elevated temperature (140-143°C ± 10°C; D.R. 1.2) with a tension generally of 8000 ± 1000. Between the third roll and fourth or last roll, yarn is drawn at a preferred temperature lower than the previous stage (135 ± 5°C) at a draw ratio of 1.15 with a tension generally of 8500 ± 1000 gm. The drawn yarn is allowed to cool under tension on the last roll before it is wound onto the winder. The drawn precursor or feed yarn has a denier of 1200, UE (ultimate elongation) 3.7%, UTS (ultimate tensile strength) 30 g/den (~ 2.5GPa) and modulus 1200 gm/den (~ 100GPa).

Example 4

Poststretching

Two precusor yarns were prepared by the method of Example 3 having properties shown in Table I, samples 1 and 4. These precursor feed yarns were cooled under greater than 4 g/d (~0.3 GPa) tension to below 80°C and at the temperature and percent stretch shown in Table I to achieve the properties shown as samples 2, 3 and 5 to 9. Samples 2 and 3 were prepared from feed or precursor yarn sample 1 and samples 5 to 9 were prepared from feed yarn 4. Stretching speed was 18 m/m across a 12 m draw zone (3 passes through a 4 m oven). Sample 9 filaments began breaking on completion of the stretching. Tension

on the yarn during stretching was between about 8.6 pounds (3.9 kg) and 11.2 pounds (5.10 kg) at 140.5°C and between about 6.3 pounds (2.86 kg) and 7.7 pounds (3.5 kg) at 149°C.

Example 5

Two-Stage Poststretching

A precursor feed yarn was prepared by the method of Example 3 having properties shown in Table II, Sample 1 and tensilized or stretched in two stages in an oven about 4 m long in four passes of 4 m each per stage (total 16 m) at 149°C to achieve properties at the stretch percent shown in Table II. Yarn was cooled below 80°C at tension over 4 g/d (0.346 GPa) before each stretch step Final take-up was about 20 m/m.

Example 6

Two Stage Poststretching of Twisted Feed Yarn

A precursor feed yarn was prepared by the method of Example 3 having properties shown in Table III, Sample 5 and tensilized (stretched) at the conditions and with the resulting properties shown in Table III. Before stretching the yarn was twisted to 3/4 twist per inch on a conventional ring twister which lowers the physical properties as can be seen in the feed yarn properties for Sample 5 of Table III. Note that modulus is then nearly doubled by the method of this invention. Final take-up was at about 20 m/m.

Example 7

Poststretched Braid

A braid was made in the conventional manner by braiding eight yarns feed (Sample 5 of Table III) yarns together. The braid had the properties given in Table IV, Sample 1 and was stretched under the conditions given in Table IV on a conventional Litzler unit to achieve the properties given in Table IV. Again modulus is about doubled or better, and tenacity increase by about 20-35%

It is comtemplated that the method of poststretching of this invention can also be applied to polyolefin tapes, film and fabric, particularly woven fabric, which have been made from high molecular weight polyolefin and previously oriented. The poststretching could be by biaxial stretching, known in the film orientation art, by use of a tenter frame, known in the textile art, or monoaxial stretching for tapes. The tape, film or fabric being poststretched should be highly oriented, or constructed of highly oriented fiber, preferably by originally orienting (e.g.. drawing) at a higher rate at a temperature near the melting point of the polymer being drawn. The poststretching should be within 5°C of the melting point of the polyolefin and at draw rate below 1 second^{-1} in at least one direction.

Creep Values for Examples 4 to 6

Room Temperature Tests

The feed precursor yarn of Example 5, Sample 1, Table II, was used as control yarnm, labeled Sample 1 in Table V for creep measurement at room temperature and a load of about 30% breaking strength (UTS). Sample 2, Table V, is a typical yarn made by the method of Example 4 and Sample 3 of Table V is Sample 2 from Table I. Note that creep values of the yarn of this invention are less than 75% or better one-half of the control yarn values at the beginning and improve to less than 25% or better after 53 hours.

Creep Tests at 71°C

In accelerated tests at 160°F (71.1°C) at 10% load the yarns of this invention have even more dramatic improvement in values over control yarn. Creep is further defined at column 15 of U.S. 4 413 110 beginning with line 6. At this temperature the yarns of the invention have only about 10% of the creep of the control values

In Table VI Sample 1 is Table I, Sample 1, Feed Yarn; Sample 2 is Table I Sample 7, yarn of this invention; as is Sample 3, which is yarn of Sample 8, Table I.

Retention of Properties at Increased Temperatures

Figure 1 shows a graphic representation of tenacity (UTS) measured at temperatures up to 145°C for three samples a control and two yarns of this invention, all tested as a bundle of ten filaments. The control yarn is typical of feed yarn, such as Sample 1 Table I. The data and curve labeled 800 denier is typical poststretched yarn, such as Sample 7, Table I and similarly 600 denier is typical two-stage stretched yarn, such as Sample 3, Table II or single stage stretched, such as Sample 2, Table II. Note that 600 denier yarn retains the same tenacity at more than about 30°C higher

temperatures than the prior art control yarn, and the 800 denier yarn retains the same tenacity at more than about 20°C higher temperatures up to above 135°C.

Shrinkage

Similarly when yarn samples are heated to temperatures up to the melting point the yarn of this invention shows much lower free - (unrestrained) shrinkage as shown in Table VII. Free shrinkage is determined by the method of ASTM D 885, section 30.3 using a 9.3 g weight, at temperatures indicated, for one minute. Samples are conditioned, relaxed, for at least 24 hours at 70°F (21.1°C) and 65% relative humidity The samples are as described above for each denier. The 400 denier sample is typical yarn from two-stage poststretching, such as Sample 5, Table II.

Annealing

Yarns of the present invention were prepared by a process of annealing and poststretching. In one precursor mode the annealing was carried out on the wound package of yarn prior to poststretching. This is "off-line" annealing. In another process the yarn was annealed "in-line" with the poststretching operation by passing the yarn through a two-stage stretch bench with minimal stretch in the first stage and maximum stretch in the second stage.

Ultra High Molecular Weight Yarn

"Off-line" Annealing

A wound roll of yarn from Example 1 described above was placed in a forced convection air oven maintained at a temperature of 120°C. At the end of 15 minutes, the yarn was removed from the oven, cooled to room temperature and fed at a speed of 4 m/min. into a heated stretch zone maintained at 150°C. The yarn was stretched 1.8/1 in traversing the stretch zone. The tensile properties, creep and shrinkage of the annealed and restretched yarn are given in Table VIII. The creep data are also plotted in Figure 2.

It will be noted that in comparison with the precursor (feed) yarn from Example 1, the annealed and restretched yarn was of 19% higher tenacity and 146% higher modulus. The creep rate at 160°F (71.1°C), 39,150 psi (2758.3 kg/cm2) was reduced to one-nineteenth of its initial value and the shrinkage of the yarn at 140°C was one-fourth of its initial value.

In comparison with the high modulus yarn of the prior art (example 548, U.S. Patent 4 413 110) the annealed and restretched yarn was of 5% higher modulus, the creep rate at 160°F (71.1°C), 39,150 psi (2758.3 kg/cm²) was about one-fifth as great (0.105%/hour v. 0.48%/hour) and the shrinkage at 140°C was lower and more uniform.

"In-line" Annealing

The ultra high molecular weight yarn sample from Example 1 described previously was fed into a two stage stretch bench at a speed of 4 m/minute. The first zone or annealing zone was maintained at a temperature of 120°C. The yarn was stretched 1.17/1 in traversing this zone; the minimum tension to keep the yarn moving. The second zone or restretching zone was maintained at a temperature of 150°C. The yarn was stretched 1.95/1 in traversing this zone. The tensile properties creep and shrinkage of the in-line annealed and restretched yarn are given in Table VIII. The creep data are also plotted in Figure 2.

It will be noted that in comparison with the precursor yarn (Example 1) the in-line annealed and restretched yarn was of 22% higher tenacity and 128% higher modulus. The creep rate at 160°F (71.1°C), 39,150 psi (2758.3 kg/cm²) was reduced to one-twenty fifth of its initial creep and the shrinkage of the yarn at 140°C was about one-eight of its initial value.

In comparison with the high modulus yarn of prior art (example 548, U.S. Patent 4 413 110), the in-line annealed and restretched yarn showed one-sixth the creep rate at 160°F (71.1°C), 39,150 psi - (2758.3 kg/cm²) (0.08%/hour v. 0.48%/hour) and the shrinkage at 140°C was about one-half as great and more uniform.

High Molecular Weight Yarn -"Off-line" Annealed

A wound roll of yarn sample from Example 2 described previously was placed in a forced convection air oven maintained at a temperature of 120°C. At the end of 60 minutes the yarn was removed from the oven, cooled to room temperature and fed at a speed of 11.2 m/minutes into a heated stretch zone maintained at 144°C. The yarn was stretched 2.4/1 in traversing the stretch zone. The tensile properties, creep and shrinkage of the annealing and restretched yarn and given in Table IX.

It will be seen that in comparison with the precursor yarn from Example 2, the annealed and restretched yarn was of 18% higher tenacity and 92% higher modulus. The creep rate of the an-

nealed and restretched yarn was comparable to the creep rate of a much higher molecular weight yarn prepared without annealing and restretching. Creep rate was 2% of the precursor yarn.

Examples 8 to 13

Several 19 filament polyethylene yarns were prepared by the method discussed in U.S. Patent 4 551 296. The starting polymer was of 26 IV - (approximately 4 x 10^6 MW). It was dissolved in mineral oil at a concentration of 6 percent by weight at a temperature of 240°C. The polymer solution was spun through a 19 filament die of 0.040" (0.1016 cm) hole diameter. The solution filaments were stretched 1.1/1 prior to quenching. The extracted gel filaments were stretched to a maximum degree at room temperature. The dried xerogel filaments were stretched at 1.2/1 at 60°C and to a maximum degree (different for each yarn) at 130°C and at 150°C. Stretching was at a feed speed of 16 m/m. The tensile properties of these first stretched yarns are given in the first column of Table X.

The first stretched yarns were annealed at constant length for one hour at 120°C. The tensile properties of the annealed yarns are given in the second column of Table X. The annealed yarns were restretched at 150°C at a feed speed of 4 m/min. The properties of the restretched yarns are given in the last column of Table X. Duplicate entries in the last column indicate the results of two separate stretching experiments.

Examples 9 to 13 are presented in Tables XI to XV.

Thus the method of the present invention provides the capability of preparing highly stable ultra-high modulus multi-filament yarns using spinning and first stretching conditions which yielded initial yarns of conventional modulus and stability.

Discussion

It is expected that other polyolefins, particularly such as polypropylene, would also have highly improved properties similar to the degree of improvement found with high molecular weight (high viscosity) polyethylene.

The superior properties of the yarn of this invention are obtained when the feed yarn has already been oriented to a considerable degree, such as by drawing or stretching of surface grown fibrils or drawing highly oriented, high molecular weight polyolefin fiber or yarn, preferably polyethylene at a temperature within 5° to 10°C of its melting point, so that preferably the fiber melt point is above 140°, then this precursor or feed yarn may be preferably cooled under tension or annealed then slowly poststretched (drawn) to the maximum without breaking at a temperature near its melt point (preferably within about 5°C to 10°C). The poststretching can be repeated until improvement in yarn properties no longer occurs. The draw or stretch rate of the poststretching should preferably be considerably slower than the final stage of orientation of the feed yarn, by a factor of preferably from about 0.1 to 0.6:1 of the feed yarn draw rate, and at a draw rate of less than 1 $second^{-1}$.

The ultra high modulus achieved in the yarn of this invention varies by the viscosity (molecular weight) of the polymer of the fiber, denier, the number of filaments and their form. For example, ribbons and tapes, rather than fibers would be expected to achieve only about 1200 g/d (~ 100 GPa), while low denier monofilaments or fibrils could be expected to achieve over about 2,400 g/d (~200 GPa). As can seen by comparing the lower viscosity polymer (lower molecular weight) fiber Example 13 with similarly processed higher viscosity polymer (higher molecular weight) fiber which has been drawn even less in poststretching in Example 10, modulus increases with molecular weight. Although mostly due to the amount of poststretching, it can be seen from the Examples that lower denier yarns of this invention exhibit higher tensile properties than do the higher denier poststretched yarns.

U.S. Patent 4 413 110 described yarns of very high modulus. The moduli of examples 543-551 exceeded 1600 g/d (133.7 GPa) and in some cases exceeded 2000 g/d (178.6 GPa). Example 548 of U.S. Patent 4 413 110 described a 48 filament yarn prepared from 22.6 IV polyethylene (approximately 3.3 x 10^6 Mw) and possessing a modulus of 2305 g/d (205 GPa). This yarn had the highest modulus of the group of examples 543-551.

The elevated temperature creep and shrinkage of this same yarn sample has been measured. Creep was measured at a yarn temperature of 160°F (71.1°C) under a sustained load of 39,150 psi (2758.3 kg/cm^2). Creep is defined as follows:

$$\% \text{ creep} = 100 \times [A(s,t) - A(o)]/A(o)$$

where

A(o) is the length of the test section immediately prior to application of load, s.

A(s,t) is the length of the test section at time t after application of load, s.

Creep measurements on this sample are presented in Table VIII and Figure 2. It will be noted that creep rate over the first 20 hours of the test averaged 0.48%/hour.

Shrinkage measurements were performed using a Perkin-Elmer TMS-2 thermomechanical analyzer in helium, at zero load, at a heating rate of 10°C/minute. Measurements of cumulative shrinkage over the temperature range room temperature to 140°C were 1.7%, 1.7% and 6.1% in three determinations.

Table XVI presents measurements of fiber viscosity (IV), modulus and creep rate [160°F - (71.1°C), 39,150 psi (2758.3 kg/cm²)] for prior art fibers including sample 2 which is example 548 of U.S. Patent 4 413 110.

The creep data of Table XVI are well correlated by the following relationship:

$$\text{Creep rate } \%/\text{hr} = 1.11 \times 10^{10} (\text{IV})^{-2.78} (\text{modulus})^{2.11}$$

In fact, as shown in Table XVII the fiber of this invention have observed, measured creep values of about 0.2 to about 0.4 (or considerably less than half) of the prior art fiber creep values, calculated by the above formula.

Table I

Sample	Denier	UE, %	UTS, g/d	Modulus g/d	Stretch Temp, °C	Stretch, %
1	1241	3.7	30.1	1458	(Feed Yarn)	
2	856	2.9	34.5	2078	140.5	45.1
3	627	2.8	37.8	2263	149.0	120.0
4	1337	3.7	29.0	1419	(Feed Yarn)	
5	889	2.8	34.9	2159	140.5	45.1
6	882	2.8	33.9	2023	140.5	50.3
7	807	2.7	35.9	2229	140.5	60.0
8	770	2.7	34.9	2130	140.5	70.0
9	700	2.7	37.4	2150	140.5	80.0
			GPa	GPa		
1			2.5	123		
2			2.9	176		
3			3.2	192		
4			2.4	120		
5			3.0	183		
6			2.9	171		
7			3.0	189		
8			3.0	180		
9			3.2	182		

Table II

Sample	Denier	UE, %	UTS, g/d	Modulus g/d	Stretch, % 1	2
1	1214	3.6	30.9	1406	(Feed	Yarn)
2	600	2.7	38.6	1953	100	none
3	570	2.7	38.2	1928	110	10
4	511	2.7	37.6	2065	110	20
5	470	2.7	40.4	2098	110	30
			GPa	GPa		
1			2.6	119		
2			3.3	165		
3			3.2	163		
4			3.2	175		
5			3.4	178		

Table III

Sample	Denier	UE, %	UTS, g/d	Modulus, g/d	Yarn Tension, lbs	Stretch, Temp	%
1	827	2.6	33	1991	10-13	140.5	50
2	769	2.6	35	2069	10-14	140.5	60
3	672	2.6	38	2075	7.5-10	149.0	80
4	699	2.6	36	1961	7.5-10	149.0	90
5	1190	3.4	29	1120	(Feed Yarn)		
			GPa	GPa	kg		
1			2.8	169	4.5-5.9		
2			3.0	175	4.5-6.36		
3			3.2	176	3.4-4.5		
4			3.0	166	3.4-4.5		
5			2.4	95			

Table IV

			g/d	g/d			
1	9940	5.0	19.4	460	(Feed Braid)		
2	8522	3.6	23.2	872	-	140.5	16
3	6942	3.2	26.8	1090	-	140.5	30
4	6670	3.2	26.2	1134	-	140.5	33
			GPa	GPa			
1			1.6	39.0			
2			1.9	73.9			
3			2.3	92.4			
4			2.2	96.1			

Table V

Room Temperature - Creep Measurement

Identification:	Sample 1 Control from Table II, Sample 1 Feed Yarn	Sample 2 One Stage Poststretch Typical of Example 4	Sample 3 Poststretched Sample 2 from Table I
Denier	1214	724	856
UE, %	3.6	2.6	2.9
UTS, g/d	30.9	34.2	34.5
GPa	2.6	2.8	2.9
Modulus, g/d	1406	2104	2078
GPa	119	178	176
Load, g/d	9.27	10.26	9.27
GPa	0.78	0.87	0.78
Creep percent after:			
10 minutes	3.9	1.7	1.4
30 minutes	4.1	1.8	1.5
1 hour	4.3	1.8	1.5
3 hours	4.6	1.9	1.6
10.5 hours	5.4	2.2	1.9
19.5 hours	6.3	2.3	2.0
34.5 hours	8.3	2.6	2.2
44.0 hours	9.7	2.8	2.3
53.5 hours	12.6	3.0	2.6
62.2 hours	broke	3.2	2.6

Table V (Continued)

Room Temperature - Creep Measurement

Identification:	Sample 4 Control, Similar to Table II Sample 1	Sample 5 Poststretched Typical 600 d. yarn	Sample 6 Poststretched Typical 800 d. yarn as in Table I, Sample 2
Denier	1256	612	804
UE, %	3.7	3.2	3.1
UTS, g/d	29.3	38.2	34.1
Modulus, g/d	1361	2355	2119
Load, percent of break strength	30	30	30
Creep percent after:			
10 minutes	3.5	1.80	2.7
30 minutes	3.1	1.94	2.8
1 hour	3.2	2.00	2.9
3 hours	3.5	2.16	3.0
3 days	7.1	3.80	4.2
4 days	8.2	4.31	4.5
5 days	9.3	4.78	4.8
7 days	11.8	5.88	5.6
10 days	16.0	7.84	6.9
11 days	18.0	8.60	7.4
12 days	19.6	9.32	7.8
13 days	21.4	10.00	8.2
14 days	23.6	10.80	8.7
15 days	broke	13.20	10.1
16 days	-	14.10	10.6

Table VI

Creep Tests at 10% Load, 71.1°C

	Sample 1	Sample 2	Sample 3	
Identification:	Feed Yarn Table I, Sample 1	Poststretched Table I, Sample 7	Poststretch Table I, Sample 8 Test 1	Retest
Denier	101	86	100	77
Load, g	315	265	312	240
Creep percent after:				
hours				
8	15	1.6	2.9	2.2
16	26	2.5	5.2	3.8
24	41	3.2	7.6	5.6
32	58	3.9	10.1	7.3
40	broke*	4.5	13.3	9.6
48		5.5		
56		6.3		
64		7.0		

* After 37 hours and after 82.9% creep.

Table VII

Free Shrinkage in Percent

Temperature, °C	Sample			
	Control	800 Denier	600 Denier	400 Denier
50	0.059	0.05	0.054	0.043
75	0.096	0.09	0.098	0.086
100	0.135	0.28	0.21	0.18
125	0.3	0.43	0.48	0.36
135	2.9, 3.4	1.4, 1.9	0.8, 0.9	-
140	5.1	2.1	1.2	-
145	22.5, 21.1	16.6, 18.0	3.2, 7.5	1.2, 1.1

Table VIII

Properties of Ultra High Modulus Yarns from Ultra High Molecular Weight Yarns

	Tenacity, g/d	Modulus, g/d	Creep Rate, %/hr *	Percent Shrinkage at 140°C**
Best Prior Art (U.S. Patent 4 413 110)				
Example 548	32.0	2305	0.48	1.7, 1.7, 6.1
Precursor Yarn				
Sample from Example 1	28.0	982	2.0	5.4, 7.7
Yarns of This Invention				
Off-line Annealed	33.4	2411	0.105	1.4, 1.7
In-line Annealed	34.1	2240	0.08	0.7, 1.0

* At 160°F (71.1°C), 39,150 psi (2758.3 kg/cm^2)

** Cumulative shrinkage between room temperature and 140°C

Table IX

Properties of Ultra High Modulus Yarns - High Molecular Weight (7 IV)

	Tenacity, g/d	Modulus, g/d	Creep Rate, %/Hr *	Percent Shrinkage at 140°C**
Precursor Yarn				
Sample from Example 2	20.3	782	120	-
Yarn of This Invention				
Off-line Annealed	23.9	1500	2.4	16.8, 17.8

* At 160°F (71.1°C), 39,150 psi (2758.3 kg/cm^2)

** Cumulative shrinkage between room temperature and 140°C

Table X

Example 8

	After First Stretch	Annealed 1 hr at 120°C	After Restretch at 150°C
Sample 1			
Denier	176	159	103, 99, 100
Tenacity, g/d	25.3	23.8	27.5, 36.6, 29.0
Modulus, g/d	1538	1415	2306, 2250, 2060
UE, %	2.6	2.4	1.8, 2.3, 2.2
Sample 2			
Denier	199	191	104, 131
Tenacity, g/d	29.5	25.2	28.4, 25.1
Modulus, g/d	1308	1272	2370, 1960
UE, %	3.2	2.9	1.7, 2.0
Sample 3			
Denier	212	197	147
Tenacity, g/d	26.0	25.0	29.0
Modulus, g/d	1331	1243	1904
UE, %	3.0	2.8	2.4
Sample 4			
Denier	1021	941	656, 536
Tenacity, g/d	30.4	29.3	35.3, 35.0
Modulus, g/d	1202	1194	1460, 1532
UE, %	3.9	3.6	3.1, 3.1
Sample 5			
Denier	975	1009	529
Tenacity, g/d	30.1	295	36.6
Modulus, g/d	1236	1229	1611
UE, %	3.8	3.7	3.2

Table XI

Annealing/Restretching Studies

Example 9

Feed: as in Example 8, 19 FILS, 26 IV, 236 denier, 29.7 g/d tenacity, 1057 g/d modulus, 4.3% UE

Restretched at 150°C with no annealing

Sample No.	Feed Speed, m/min	Stretch Ratio at 150°C	Denier	UTS Tenacity, g/d	Modulus, g/d	UE, %
1	4	1.5	128	30.8	1754	2.6
2	8	1.5	156	28.6	1786	2.4
3	16	1.3	177	27.8	1479	2.7

Restretched at 120°C and 150°C

Sample No.	Feed Speed m/min	Stretch Ratio at 120°C	150°C	Denier	UTS Tenacity, g/d	Modulus, g/d	UE, %
4	4	1.15	1.5	158	30.6	1728	2.8
5	8	1.13	1.27	192	32.8	1474	3.2
6	16	1.18	1.3	187	29.3	1462	3.0

Annealed 1 hour at 120°C, Restretched at 150°C

Sample No.	Feed Speed, m/min	Stretch Ratio at 150°C	Denier	UTS Tenacity, g/d	Modulus, g/d	UE, %
7	4	1.8	131	32.4	1975	2.3
8	8	1.35	169	31.2	1625	2.6
9	16	1.3	185	29.3	1405	3.0

Table XII

Annealing/Restretching Studies

Example 10

Feed: as in Example 8, 19 FILS, 26 IV, 258 denier, 28.0 g/d tenacity, 982 g/d modulus, 4.1% UE

Annealed in-line

Sample No.	Feed Speed, m/min	Stretch Ratio at T.	Stretch Ratio 150°C	Denier	Tenacity, g/d	Modulus, g/d	UE, %
Annealed in-line at 120°C							
1	4	1.17	1.95	114	34.1	2240	2.2
2	8	1.18	1.6	148	33.0	1994	2.6
Annealed in-line at 127°C							
3	4	1.18	1.75	124	33.0	2070	2.6
4	8	1.17	1.3	173	32.0	1688	2.6
Annealed in-line at 135°C							
5	4	1.17	1.86	129	36.0	2210	2.4
6	8	1.17	1.5	151	31.9	2044	2.4

Annealed off-line (restretched at 4 m/min)

Sample No.	Annealed Temp, °C	Annealed Time, min	Stretch Ratio at 150°C	Denier	Tenacity, g/d	Modulus, g/d	UE, %
1	120	15	1.8	102	33.4	2411	2.3
2	120	30	1.9	97	29.2	2209	2.2
3	120	60	1.8	109	32.6	2243	2.4
1	130	15	1.8	111	32.4	2256	2.4
2	130	30	1.7	125	32.5	2200	2.1
3	130	60	1.5	136	28.9	1927	2.7

Table XIII

Annealing/Restretching Study

Example 11

Feed: similar to Example 2 but: 118 FILS, 26 IV, 1120 denier, 30.0 g/d tenacity, 1103 g/d modulus

Annealed in-line, 3 passes x 3 meters, restretched at 150°C, restretched at 8 m/min feed speed

Sample No.	T.,°C	Stretch Ratio at T.	Stretch Ratio at 150°C	Tension, lbs No. 1	Tension, lbs No. 2
Hot Feed Roll					
1	149	1.02	1.45	0.98	0.54
2	151	1.65	1.27	3.08	0.92
3	151	1.33	1.32	-	-
4	140	0.96	1.6	1.02	0.72
5	140	1.25	1.35	4.42	0.84
6	140	1.10	1.41	3.50	1.10
7	131	0.99	1.48	1.94	0.82
8	130	1.37	1.30	9.58	1.00
9	130	1.16	1.39	8.68	0.92

Sample No.	Denier	UTS Tenacity, g/d	Modulus, g/d	UE, %
Hot Feed Roll				
1	662	33.1	1730	3.0
2	490	36.4	1801	2.8
3	654	34.3	1801	2.9
4	742	32.0	1422	3.3
5	588	35.5	1901	2.8
6	699	34.1	1750	3.0
7	706	31.8	1501	3.1
8	667	33.9	1744	2.8
9	706	33.6	1603	3.1

Table XIII (Continued)

Cold Feed Roll

Sample No.	T.,°C	Stretch Ratio at T.	Stretch Ratio at 150°C	Tension, lbs No. 1	Tension, lbs No. 2
10	150	0.94	1.50	0.7	0.72
11	149	1.11	1.42	2.04	0.76
12	150	1.31	1.30	3.36	0.44
13	150	1.50	1.25	4.12	0.56
14	150	1.66	1.18	4.68	0.24
	150	1.84(broke)	1.16	-	-
15	140	1.03	1.45	-	-
16	140	1.48	1.25	4.46	1.00
17	130	1.06	1.53	1.15	-
18	130	1.43	1.22	7.94	1.24
19	120	0.96	1.68	0.86	-
20	120	1.07	1.40	5.86	0.94

Sample No.	Denier	UTS Tenacity, g/d	Modulus, g/d	UE, %
10	685	34.2	1606	3.2
11	724	33.4	1677	3.1
12	609	34.1	1907	2.7
13	613	35.2	1951	2.7
14	514	35.8	2003	2.6
15	741	33.6	1545	3.3
16	641	35.8	1871	2.8
17	640	31.8	1391	3.1
18	669	33.6	1813	2.8
19	707	29.6	1252	3.2
20	694	33.1	1690	3.0

Annealed 15 min at 120°C

Sample No.	T.,°C	Stretch Ratio at T.	Stretch Ratio at 150°C	Tension, lbs No. 1	Tension, lbs No. 2
21(outside)	150	1.61	1.21	-	-
22(inside)	-	-	-	-	-

Sample No.	Denier	UTS Tenacity, g/d	Modulus, g/d	UE, %
21(outside)	538	36.8	2062	2.6
22(inside)	562	35.2	1835	2.7

Table XIV

Annealing/Restretching Study

Example 12

Annealed on roll 1 hour at 120°C restretched in two stages at 150°C - (restretch feed speed = 8 m/min)

Sample No.	Stretch Ratio No. 1	Stretch Ratio No. 2	Denier	Tenacity, g/d	Modulus, g/d	UE, %
1	Control		1074	31.2	1329	-
2	1.65	1.21	567	38.5	1948	2.8
3	1.62	1.18	546	39.7	2005	2.8
4	Control		1284	30.0	1309	3.6
5	1.66	1.21	717	35.8	1818	2.7
6	1.65	1.16	668	37.3	1797	2.8
7	1.63	1.17	683	37.3	1904	2.8
8	1.62	1.14	713	36.6	1851	2.8
9	1.62	1.15	700	37.0	1922	2.8
10	Control		1353	29.0	1167	3.7
11	1.61	1.14	660	36.6	1949	2.7
12	1.62	1.16	752	36.2	1761	2.9

5

Table XV

Restretching of 7 IV Yarns from Example 2

Example 13

118 FILS

Annealing Time at 120°C	Restretch Ratio at 144°C	Denier	Tenacity, g/d	Modulus, g/d	UE, %
Control		347	20.5	710	4.8
0	2.2	140	21.4	1320	2.4
0	2.4	140	22.3	1240	2.7
0	2.75	133	23.0	1260	2.6
Control		203	20.3	780	4.7
60 minutes	2.2	148	22.8	1280	2.8
60 minutes	2.4	112	23.9	1500	2.6
60 minutes	2.75	116	22.4	1500	2.4
60 minutes	2.88 (broke)	75	22.1	1670	1.9

Table XVI

Prior Art Fibers

Sample No.	Fiber Viscosity (IV) dl/g	Modulus g/d	Creep Rate at 160°F, 39,150 psi, %/hr Observed	Calculated*
1	6.5	782	44	48
			54	48
2	13.9	2305	0.48	0.60
3	15.8	1458	1.8	1.1
4	16.9	982	1.6	2.1

* Creep Rate = 1.1144×10^{10} (IV)$^{-2.7778}$ (Modulus)$^{-2.1096}$

55

Table XVII
Fibers of the Invention

Sample No.	Fiber Viscosity (IV) dl/g	Modulus g/d	Creep Rate at 160°F 39,150 psi, %/hr Observed	Calculated*	Obs/Calc
1	6.5	1500	2.4	12.6	0.19
2	14.6	2129	0.10	0.62	0.16
3	16.9	2411	0.10	0.32	0.31
4	16.9	2204	0.08	0.38	0.21
5	17.9	2160	0.14	0.34	0.41

* Calculated from relationship for prior art fibers
Creep Rate = 1.11×10^{10} $(IV)^{-2.8}$ $(Modulus)^{-2.1}$

Claims

1. A polyolefin shaped article having a creep rate, measured at 160°F (71.1°C) and 39,150 psi - (2758.3 kg/cm²) load, less than one-half that value given by the following equation:

per cent/hr = 1.11×10^{10} $(IV)^{-2.78}$ $(Modulus)^{-2.11}$

where IV is the intrinsic viscosity of the article measured in decalin at 135°C, dl/g, and Modulus is the tensile modulus in grams per denier of the article measured by ASTM 885-81 at 110%/minute strain rate, zero strain.

2. The article of claim 1 wherein the article is a fiber.

3. The article of claim 1 wherein the polyolefin is polyethylene.

4. The article of claim 3 wherein the article is a fiber.

5. A high strength, high modulus, low creep, high molecular weight polyethylene fiber which has been poststretched to achieve at least about a ten percent increase in tensile modulus and at least about a twenty percent decrease in creep rate measured at 160°F (71.1°C) under 39,150 psi - (2758.3 kg/cm²) load.

6. A high strength, high modulus, low creep, high molecular weight, polyethylene fiber which has been poststretched to achieve at least about a twenty percent decrease in creep rate measured at 160°F (71.1°C) under 39,150 psi (2758.3 kg/cm²) load, and a retention of the same tenacity as the same fiber, before poststretching, at a temperature at least about 15°C higher.

7. The fiber of claim 5 wherein total fiber shrinkage measured at 135°C is less than about 2.5 percent.

8. The fiber of claim 6 wherein total fiber shrinkage measured at 135°C is less than about 2.5 percent.

9. The fiber of claim 5 wherein the weight average molecular weight of the fiber is at least about 800,000 and the tenacity is at least about 32 grams per denier.

10. The fiber of claim 6 wherein the weight average molecular weight of the fiber is at least about 800,000 and the tenacity is at least about 32 grams per denier.

11. The fiber of claim 5 wherein the weight average molecular weight of the fiber is at least about 250,000 and the tenacity is at least about 20 grams per denier.

12. The fiber of claim 6 wherein the weight average molecular weight of the fiber is at least about 250,000 and the tenacity is at least about 20 grams per denier.

13. The fiber of claim 7 wherein the weight average molecular weight of the fiber is at least about 800,000 and the tenacity is at least about 32 grams per denier.

14. The fiber of claim 8 wherein the weight average molecular weight of the fiber is at least about 800,000 and the tenacity is at least about 32 grams per denier.

15. The fiber of claim 7 wherein the weight average molecular weight is at least about 250,000 and the tenacity is at least about 20 grams per denier.

16. The fiber of claim 8 wherein the weight average molecular weight is at least about 250,000 and the tenacity is at least about 20 grams per denier.

17. The fiber of claim 6 wherein the poststretched fiber has about a ten percent increase in tensile modulus.

18. The fiber of claim 17 wherein fiber shrinkage measured at 135°C is less than about 2.5 percent.

19. The fiber of claim 17 wherein the weight average molecular weight of the fiber is at least about 800,000 and the tenacity is at least about 32 grams per denier.

20. The fiber of claim 17 wherein the weight average molecular weight of the fiber is at least about 250,000 and the tenacity is at least about 20 grams per denier.

21. The fiber of claim 18 wherein the weight average molecular weight of the fiber is at least about 800,000 and the tenacity is at least about 32 grams per denier.

22. The fiber of claim 18 wherein the weight average molecular weight of the fiber is at least about 250,000 and the tenacity is at least 20 grams per denier.

23. A high strength, high modulus, low creep, high molecular weight polyethylene fiber which has been poststretched to achieve at least about a ten percent increase in tensile modulus and a retention of the same tenacity as the same fiber, before poststrectching, at a temperature at least about 15°C higher.

24. A high strength, high modulus, low creep, high molecular weight polyethylene fiber which has been poststretched to achieve at least about a ten percent increase in tensile modulus and total fiber shrinkage measured at 135°C of less than about 2.5 percent.

25. A high strength, high modulus, low creep, high molecular weight polyethylene fiber which has been poststretched to achieve at least about a ten percent increase in tensile modulus and the weight average molecular weight of the fiber is at least about 800,000 and the tenacity is at least about 32 grams per denier.

26. A high strength, high modulus, low creep, high molecular weight polyethylene which has been poststretched to achieve about a ten percent increase in tensile modulus and the weight average molecular weight of the fiber is above about 250,000 and the tenacity is at least about 20 grams per denier.

27. The fiber of claim 25 wherein the fiber retains the same tenacity as the same fiber, before poststretching, at a temperature at least about 15°C higher.

28. The fiber of claim 26 wherein the fiber retains the same tenacity as the same fiber, before poststretching, at a temperature of at least about 15°C higher.

29. A high strength, high modulus, low creep, low shrink, high molecular weight polyethylene, poststretched multifilament fiber having a weight average molecular weight at least about 800,000, tensile modulus at least about 1600 grams per denier and total fiber shrinkage less than 2.5 percent at 135°C and wherein said fiber retains the same tenacity as the same fiber, before it is poststretched, at a temperature at least about 25°C higher.

30. The fiber of claim 29 wherein said fiber also has creep of less than 0.48 percent/hour at 160°F (71.1°C), 39,150 psi (2758.3 kg/cm^2).

31. The fiber of claim 29 wherein said fiber also has a tenacity of at least about 32 grams per denier.

32. The fiber of claim 29 wherein said fiber also retains the same tenacity as the same fiber, before it is poststretched, at a temperature at least about 15°C higher.

33. A high strength, high modulus, low creep, low shrink, high molecular weight polyethylene, poststretched fiber having a weight average molecular weight of at least about 250,000 and tensile modulus of at least about 1200 grams per denier.

34. The fiber of claim 33 wherein the tenacity is at least about 20.

35. A method to prepare a low creep, high modulus, high strength, low shrink, high molecular weight polyethylene fiber having improved strength retention at high temperatures comprising

drawing a highly oriented, high molecular weight polyethylene fiber at a temperature within 10°C of its melting temperature, then

poststretching said fiber at a drawing rate of less than about 1 second^{-1} also at a temperature within 10°C of its melting temperaturing, and

cooling said fiber under tension sufficient to retain its highly oriented state.

36. The method of claim 35 wherein said fiber was first formed by solution spinning.

37. The method of claim 35 wherein the fiber is poststretched at a temperature of between about 140° to 153°C.

38. The method of claim 35 wherein said drawing is within 5°C of said fiber melting temperature.

39. The method of claim 35 wherein said poststretching is within 5°C of said fiber melting temperature.

40. The method of claim 35 wherein both said drawing and said poststretching are within 5°C of said fiber melting temperature.

41. The method of claim 35 whereby said poststretched fiber has an increased modulus of at least about 10 percent and at least about 20 percent less creep at 160°F (71.1°C) and 39,150 psi - (2758.3 kg/cm²) load than tne unstretched fiber.

42. The method of claim 35 wherein said fiber is cooled before poststretching under tension sufficient to retain its highly oriented state.

43. The method of claim 35 wherein the tension is at least 2 grams per denier.

44. The method of claim 39 wherein the tension is at least 2 g/d.

45. The method of claim 35 wherein the cooling is to at least 90°C.

46. The method of claim 39 wherein the cooling is to at least 90°C.

47. The method of claim 35 wherein said fiber is annealed after cooling but before poststretching at a temperature of between about 110° and 150°C, for a time of at least about 0.2 minutes.

48. The method of claim 47 wherein the temperature is betweeen about 110° and 150°C for a time of between about 0.2 and 200 minutes.

49. The method of claim 35 wherein the poststretching is repeated at least once.

50. A method to prepare a low creep, high modulus, low shrink high strength, high molecular weight polyolefin shaped article or fabric having improved strength retention at high temperatures, comprising

poststretching said shaped article at a drawing rate of less than about 1 second^{-1} at a temperature within 10°C of the polyolefin melting point, and

cooling said shaped article under tension sufficient to retain its highly oriented state, said shaped article prior to poststretching being fabricated from polyolefin which had been highly oriented at a higher rate than 1 second^{-1} and at a temperature of within about 10°C of its melting point.

51. The method of claim 50 wherein said poststretching is within 5°C of said polyolefin melting point.

52. The method of claim 50 wherein said orientation is within 5°C of said polyolefin melting point.

53. The method of claim 50 wherein said poststretching and said orientation are within 5°C of said polyolefin melting point.

54. A low creep, high modulus, high strength, low shrink, high molecular weight polyolefin shaped article or fabric having improved strength retention at high temperatures which has been prepared by poststretching at a drawing rate of less than about 1 second^{-1} at a temperature within about 10°C of its melting temperature, said shaped article or fabric, prior to being poststretched, being fabricated from polyolefin which had been highly oriented at a higher rate than 1 second^{-1} and at a temperature of within about 10°C of its melting point.

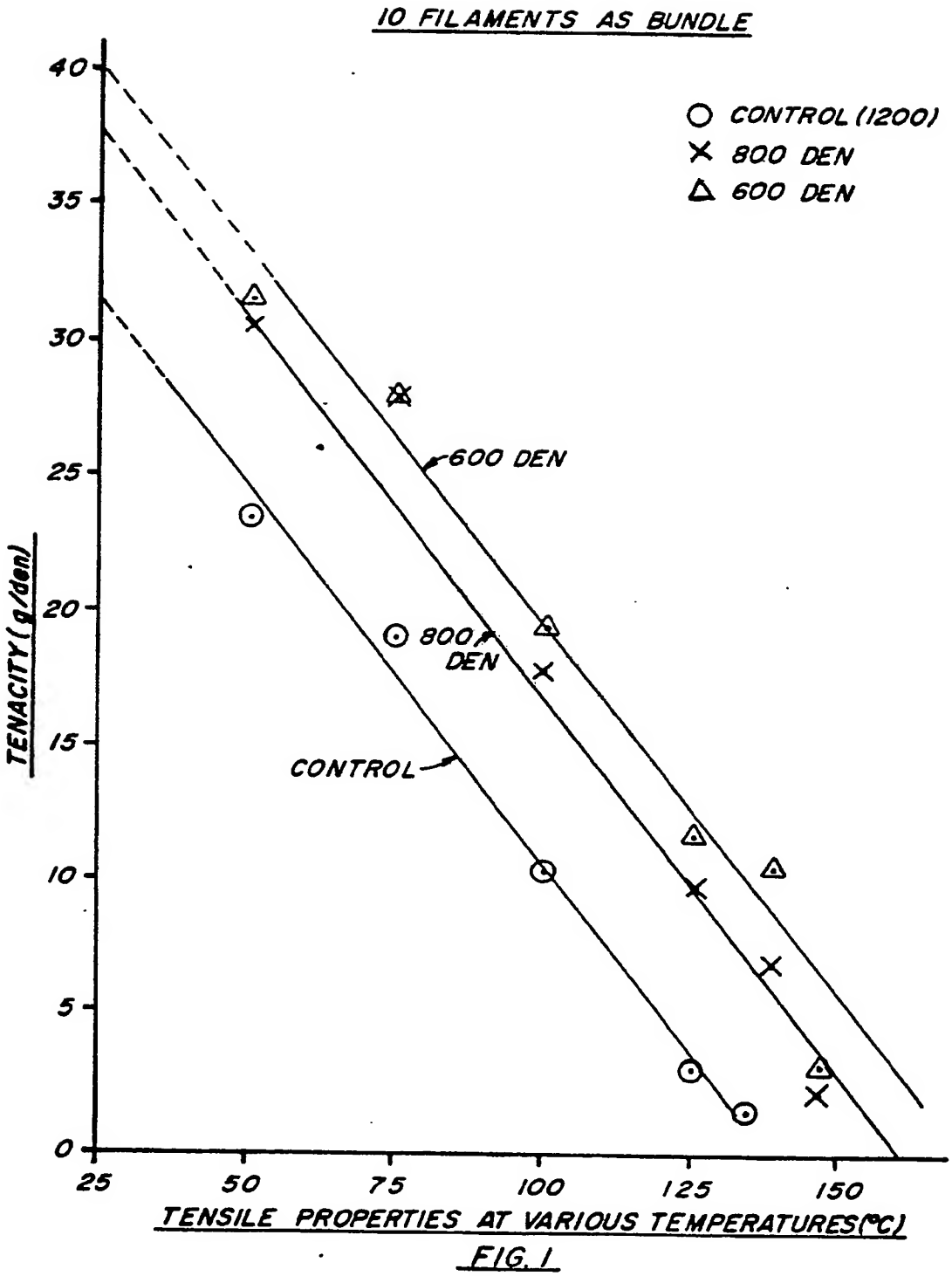


FIG. 1

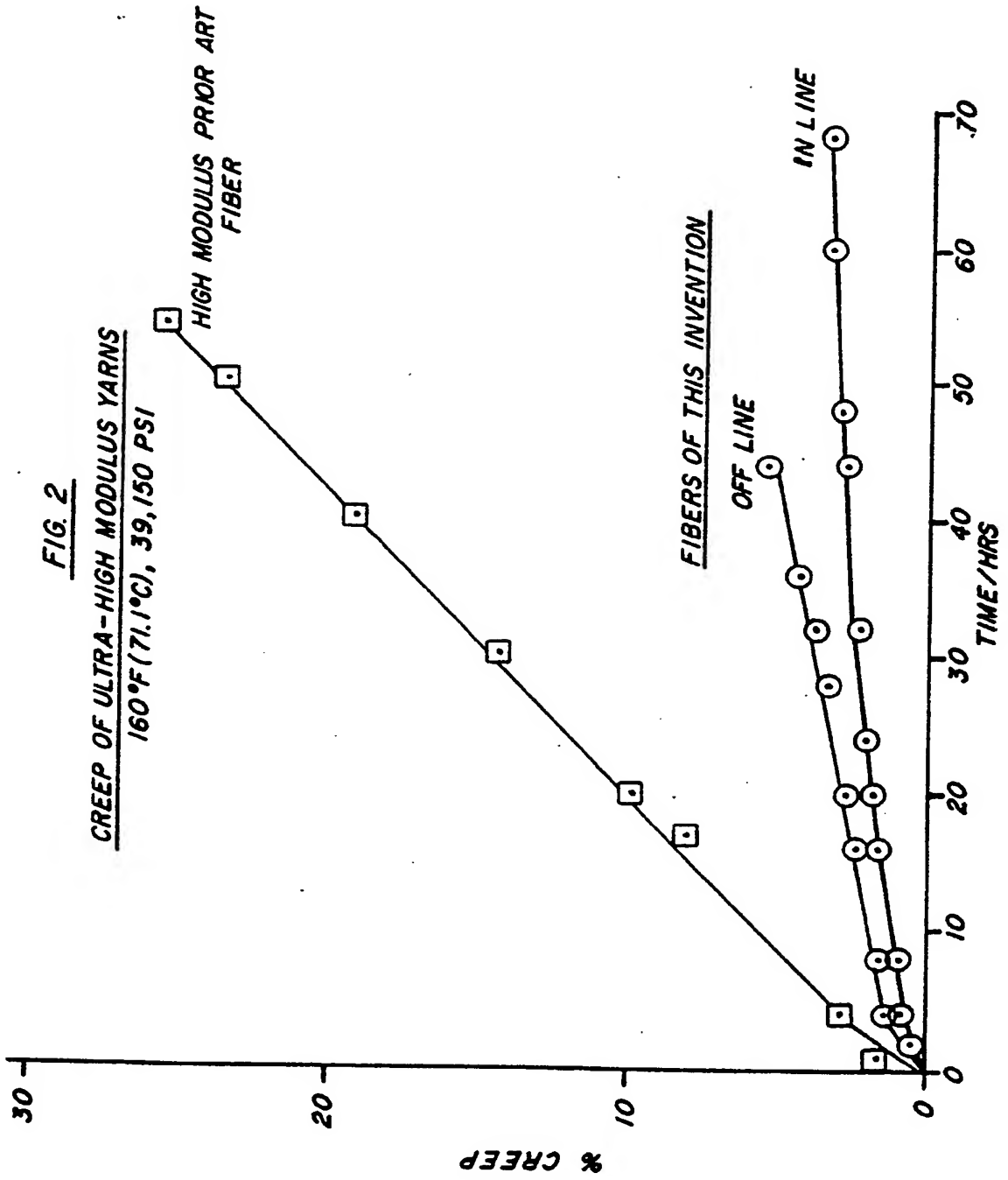


FIG. 2

CREEP OF ULTRA-HIGH MODULUS YARNS
160°F(71.1°C), 39,150 PSI

BLANK PAGE

(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 205 960**
A3

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **86107119.9**

(51) Int. Cl.⁴: **D01F 6/04** , D02J 1/22

(22) Date of filing: **26.05.86**

(30) Priority: **17.06.85 US 745164**

(43) Date of publication of application:
30.12.86 Bulletin 86/52

(84) Designated Contracting States:
DE FR GB IT NL

(88) Date of deferred publication of the search report:
07.01.88 Bulletin 88/01

(71) Applicant: **ALLIED CORPORATION**
Columbia Road and Park Avenue P.O. Box 2245R (Law Dept.)
Morristown New Jersey 07960(US)

(72) Inventor: **Dunbar, James Jay**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Kavesh, Sheldon (NMN)**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Prevorsek, Dusan Ciril**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Tam, Thomas Yiu-Tai**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Weedon, Gene Clyde**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)
Inventor: **Winckihofer, Robert Charles**
c/o Allied Corporation P.O. Box 2245R
Morristown New Jersey 07960(US)

(74) Representative: **Brock, Peter William**
UOP Processes International Corporation 48 Leicester Square
London WC2H 7LW(GB)

(54) **Very low creep, ultra high modules, low shrink, high tenacity polyolefin fiber having good strength retention at high temperatures and method to produce such fiber.**

(57) By poststretching, at a temperature between about 135° and 160°C, a polyethylene fiber, which has already been oriented by drawing at a temperature within 5°C of its melting point, an ultra high modulus, very low creep, low shrink, high tenacity polyolefin fiber having good strength retention at high temperatures is obtained. The poststretching can be in multiple stages and/or with previous annealing. The poststretching should be done at a draw rate of less than 1 second^{-1}. Tensile modulus values over 2,000 g/d (178.6 GPa) for multifilament yarn are consistently obtained for ultrahigh molecular weight polyethylene, with tensile strength values above 30 g/d (2.5 GPa) while at the same time dramatically improving creep [at 160°F (71.1°C) and 39,150 psi (2758.3 kg/cm^2) load] by values at least 25% lower than fiber which has not been poststretched. Shrinkage is improved to values less than 2.5% of the original length when heated from room temperature to 135°C. Performance at higher temperature is improved by about 15° to 25°C.

EP 0 205 960 A3

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86 10 7119

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl.4)
D,Y	GB-A-2 051 667 (STAMICARBON) * Page 2, lines 75-79,103-111 *	35-53	D 01 F 6/04 D 02 J 1/22
D,Y	EP-A-0 064 167 (ALLIED CORP.) * Claim 1 *	35-53	
A	EP-A-0 135 253 (MITSUI PETROCHEMICAL INDUSTRIES, LTD) * Page 21, line 35 *	35-53	
A	US-A-3 210 452 (W.H. HOWARD) * Claims; column 1, lines 60-64; column 2, lines 1-6 *	35-53	

TECHNICAL FIELDS SEARCHED (Int. Cl.4)

D 01 F
D 01 D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	09-10-1987	VAN GOETHEM G.A.J.M.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO Form 1503 03.82